

BIOMASS PRODUCTION AND WATER QUALITY IN AN ACIDIC SPOIL AMENDED WITH $Mg(OH)_2$ -ENRICHED BY-PRODUCT GYPSUM

Humberto Yibirin, R.C. Stehouwer, J. Bigham, and P. Sutton.
OARDC/School of Natural Resources, Williams Hall
Wooster, OH 44691

Keywords: GYPSUM, MAGNESIUM, SPOIL, LAND RECLAMATION

Gypsum (G) and $Mg(OH)_2$ (FGD-Mg) are recovered from the thickener overflow of an experimental wet FGD scrubber in the Zimmer power plant of CInergy (Cincinnati Gas and Electric Company). The purity of recovered G ranges from almost 100 to 92%, with impurities occurring mainly as $Mg(OH)_2$. Gypsum contaminated with $Mg(OH)_2$ is referred to as $Mg(OH)_2$ -enriched by-product gypsum (Mg-G).

Because of its $Mg(OH)_2$ content, Mg-G can potentially be used as a source of both Ca and Mg for green plants growing on soils and spoils with low levels of available Ca and Mg. In addition, the presence of $Mg(OH)_2$ should allow Mg-G to be used as an alkaline amendment for the reclamation of hyper-acid spoils. The total abandoned surface coal mined land needing reclamation in eastern USA has been estimated to be more than 0.5 million ha (Sutton and Dick, 1987). Gypsum can reduce Al toxicity by: (1) increased ratio of Ca to Al in the soil solution (Kinraide et al., 1992), and (2) physical removal of Al from the soil profile through Ca exchange (Wendell and Ritchey, 1993). The $Mg(OH)_2$ in Mg-G may enhance the effectiveness of these mechanisms for amelioration of phytotoxic conditions below the zone of incorporation. The presence of Mg and sulfate increases the potential for salt loading (Stehouwer et al., 1995), which may enhance downward movement of Ca and Al.

The purpose of this greenhouse study was to investigate the effects of G and Mg-G, at three application rates, on spoil and leachate pH and electrical conductivity (EC), and movement of major and trace elements. Preliminary observations on plant growth are also reported.

MATERIALS AND METHODS

Acidic minespoil was sampled from the upper 20 cm of an abandoned mineland (AML) site located at the Eastern Ohio Resource Development Center (EORDC). The samples were air-dried and passed through a 12.7-mm sieve. Initial Bray #1 P was 25 mg kg^{-1} ; NH_4 -acetate extractable Ca, K, Mg, and Al were 225, 54, 37, and 601 mg kg^{-1} respectively; CEC was 30 cmol. kg^{-1} , and pH was 2.9.

Three by-product materials were used: G (98% gypsum), and two Mg-G blends (4%Mg-G, and 8% Mg-G) which contained 4 and 8% (w/w) $Mg(OH)_2$ equivalent. Reagent grade $Ca(OH)_2$ was also mixed with G to produce two mixtures (4%Ca-G, and 8%Ca-G) with neutralizing potentials equal to 4%Mg-G and 8% Mg-G respectively.

Spoil material (8 kg) was poured into PVC columns (60 cm tall, 15 cm diam.) to a height of 36 cm forming an untreated sub-surface layer. A 15-cm surface layer of spoil (3.4 kg) was then thoroughly mixed with the various treatments and placed over the untreated spoil. The columns were mounted on flat PVC plates with a nipple in the center to allow for leachate collection.

Treatments consisted of G, 4%Mg-G, 8%Mg-G, 4%Ca-G, or 8%Ca-G applied at rates equivalent to 145, 290, and 580 Mg ha^{-1} . These rates were calculated to supply Ca from G in amounts equal to 2.5, 5.0, and 10.0 times the spoil CEC in the treated layer. Control treatments included unamended spoil and spoil amended to pH 7.0 with limestone (112 Mg ha^{-1}). Treatments were arranged in randomized complete blocks with three replications. Fertilizers were applied together with the treatments in amounts of 0.5 g NH_4NO_3 , 0.4 g triple superphosphate, and 2 g KCl.

Columns were then leached with 2.5 L of deionized water and the first leachates (150-200 ml) were collected. Following this first leaching, 5 g of soil was collected from the surface 5-cm depth of each column for pH and EC measurements, and each column was planted with 30 seeds of Orchardgrass (*Dactylis glomerata* L.). After an initial 80-d growing period, orchardgrass was harvested monthly for a total of 4 harvests. Leachates were also collected at the end of the study. Columns were watered daily with deionized water such that the amount of water applied during the study was equivalent to the average annual rainfall for SE Ohio (≈ 1000 mm).

Leachates were analyzed for pH, EC, and for As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, and Zn by inductively coupled plasma emission spectrometry. Data analysis was conducted using analysis of variance procedures, and single degree of freedom orthogonal contrasts.

RESULTS AND DISCUSSION

The Mg-G and Ca-G amendments were equally effective at increasing the pH of the acidic minespoil in the treated layer (Table 1). None of the amendments used, however, increased the pH of the first or final leachates compared to the untreated spoil. Increases in spoil pH led to increased growth of orchardgrass, however, the largest application rates of 4% and 8% Mg-G suppressed yield in the first two harvests. This initial yield suppression was associated with large increases in EC.

Mg-G increased spoil and leachate EC more than any other treatment (Table 1). The use of 4%Mg-G increased spoil EC 1.23 times compared to 4%Ca-G, 8%Ca-G, or gypsum, and 3.4 times compared to either the untreated or limed spoil. These differences were larger when the spoil was amended with 8%Mg-G. Leaching of salts out of the column during the course of the study reduced the EC in the final leachates, but Mg-G effects on EC were still present. Stehouwer et al. (1995) showed that the solubility of Mg in a spoil amended with materials containing CaSO_4 and $\text{Mg}(\text{OH})_2$ may be controlled by epsomite ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) which is ≈ 300 times more soluble than gypsum. Enrichment of gypsum with Mg, therefore, increased the potential for salt loading. Gypsum-containing treatments increased the leachate concentrations of Ca, Mg, Al, Fe, Mn, and S (Table 2), and of Cd, Cr, Pb, Cu, and B (Table 3) relative to the control treatments. The largest increase occurred with Mg-G. Most cations were much less mobile with limestone and Ca-G treatments. The use of G alone increased the movement of Al, S, Fe, Mn, Cr, and B compared to Ca-G. The $\text{Ca}(\text{OH})_2$ in Ca-G reduced the movement of metal cations in the spoil compared to G alone, thus making Ca-G behave more like limestone than G. By contrast, the $\text{Mg}(\text{OH})_2$ in Mg-G increased the movement of metal cations in the spoil compared to G alone, limestone, or Ca-G. Effects of Mg-G on cation movement were most likely not due to pH differences since Mg-G and Ca-G had similar effects on pH. The increased transport of these metals with Mg-G appeared to be due to large concentrations of Mg^{2+} in solution. We believe the increases in metals in the leachates were due to mobilization of metals present in the spoil. These were brought into solution through exchange reactions with Mg^{2+} and then transported downward.

Amendment with Mg-G increased pH, thus allowing revegetation of otherwise phytotoxic spoils. In addition to being a source of Ca and Mg, Mg-G enhanced downward movement of Al, and Fe which may promote root penetration in untreated subsurface layers, and improve the chances of reclamation success. Amendment applications, however, should be limited to rates that will not cause phytotoxic salt concentrations, excessively high pH, or increase the concentrations of heavy metals in water to harmful levels.

Table 1. Initial and final electrical conductivity (EC) and pH in the spoil and leachate, averaged across rates, as affected by wet FGD Mg(OH)₂-enriched gypsum, gypsum, Ca(OH)₂-enriched gypsum, and calcitic limestone¹.

	Spoil Init	Leach First	Leach Final	Spoil Init	Leach First	Leach Final
	----- pH -----			-----EC, S m ⁻¹ -----		
4%Mg-G	5.60	2.27	2.58	0.27	0.64	0.32
8% Mg-G	7.31	2.26	2.67	0.32	0.64	0.29
4%Ca-G	5.82	2.27	2.55	0.23	0.44	0.24
8%Ca-G	7.23	2.26	2.55	0.21	0.47	0.21
Gypsum	3.09	2.26	2.60	0.22	0.53	0.28
Untreated	2.87	2.33	2.78	0.07	0.30	0.09
Limestone	7.09	2.33	2.71	0.09	0.30	0.10
avg.	5.71	2.27	2.61	0.23	0.52	0.25
lsd 0.05 [†]	0.31	NS	0.05	0.03	0.09	0.04

[†] lsd = least significant difference.

* leachate and initial are abbreviated as leach and init.

Table 2. Major element composition of first leachate, averaged across rates, as affected by wet FGD Mg(OH)₂-enriched gypsum, gypsum, Ca(OH)₂-enriched gypsum, and calcitic limestone.

	Ca	Mg	Al	Fe	Mn	S
	----- mg L ⁻¹ -----					
4%Mg-G	124	301	866	142	3	1821
8% Mg-G	105	249	950	150	3	1903
4%Ca-G	64	53	418	72	2	646
8%Ca-G	69	56	432	76	2	617
Gypsum	78	108	700	114	3	1201
Untreated	40	35	227	48	1	440
Limestone	36	37	246	53	1	479
avg.	82	139	622	104	2	1146
lsd [†] 0.05	22	57	170	22	1	258

[†] lsd = least significant difference.

Table 3. Trace element composition of first leachate, averaged across rates, as affected by wet FGD Mg(OH)₂-enriched gypsum, gypsum, Ca(OH)₂-enriched gypsum, and calcitic limestone.

	As	Cd	Cr	Pb	Cu	B
	----- mg L ⁻¹ -----					
4%Mg-G	<0.04	0.05	0.28	0.22	0.64	4.41
8% Mg-G	<0.04	0.05	0.30	0.21	0.65	3.91
4%Ca-G	<0.04	0.04	0.14	0.11	0.50	0.40
8%Ca-G	<0.04	0.04	0.15	0.09	0.52	0.35
Gypsum	<0.04	0.05	0.24	0.18	0.63	1.30
Untreated	<0.04	0.03	0.09	0.08	0.35	0.27
Limestone	<0.04	0.03	0.08	0.19	0.32	0.23
avg.	<0.04	0.05	0.21	0.16	0.56	1.86
lsd [†] 0.05	NS	0.01	0.05	0.08	0.1	0.7

[†] lsd = least significant difference.

ACKNOWLEDGMENT

This study is part of an ongoing research program conducted at The Ohio State University. Support for this research was provided by The Ohio Coal Development Office, CInergy (Cincinnati Gas & Electric Co.), and Dravo Lime Company.

LITERATURE CITED

- Kinraide, T.B., P.R. Ryan, and L.V. Kochian. 1992. Interactive effects of Al^{3+} , H^+ , and other cations on root elongation considered in terms of cell-surface electrical potential. *Plant Physiol.* 99:1461-1468.
- Stehouwer, R.C, P. Sutton, R.K. Fowler, and W.A. Dick. 1995. Minespoil amendment with dry flue gas desulfurization by-products: Element solubility and mobility. *J. Environ. Qual.* 24:164-174.
- Sutton, P., and W.A. Dick. 1987. Reclamation of acidic mined lands in humid areas. *Adv. Agron.* 41:377-405.
- Wendell, R.R., and K.D. Ritchey. 1993. Use of high-gypsum flue gas desulfurization by-products in agriculture, p. 40-45. In Shiao-Hung (ed.), *Proceedings of the Tenth Annual International Pittsburgh Coal Conference*. September 20-24, 1993. Pittsburgh, PA.

This page left intentionally blank.